

Novel Liquid/Oligomer Hybrid Electrolyte with High Lithium-Ion Transference Number (Hi-LiT) for Extreme Fast Charging

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Overview

Timeline

- Project Start: 8/15/18
- Project End: 8/14/19
- Percent Complete: 33%

Budget

- \$50k in FY18
- \$500k in FY19
- \$450k in FY20

Barriers

- Barriers addressed
 - reducing the production cost of a BEV cell to \$80/kWh, increasing the range of BEVs to 300 miles, and decreasing the charging time to 15 minutes or less.

Collaborations

- Interactions/Collaborations
 - Guangsheng Zhang (UAHuntsville)
 - Feng Lin, Michael Schulz (Virginia Tech.)
 - Kejie Zhao (Purdue University).
 - Jue Liu (SNS, ORNL).
- Project Lead: ORNL
- Project Partner: XALT Energy

Objectives & Relevance

- **Main Objective**: To implement a novel high-Li-ion-transference (Hi-LiT) electrolyte and enable a 10-minute charge of cells with 180 Wh/kg energy density by increasing t_{Li^+} from 0.36 to 0.75 while maintaining a relatively high conductivity of 4-10 mS/cm.
- **Relevance to Barriers and Targets**
- At high charge rate, Li ion concentration gradient builds up and leads to Li ion depletion in graphite electrode.
 - Li plating, especially Li dendrite growth, leading to poor cycling performance.
 - Abruptly end the charge step, leading to low energy density.
 - Increase cell temperature, leading to electrolyte degradation and poor cycling.
- The proposed technology is to implement a novel non-aqueous electrolyte system with high Li ion transference number (Hi-LiT) for high energy density Li-ion cells. It will meet the battery performance target of delivering 180 Wh/kg of stored energy to the cell during 10-minute charging at the beginning of life and achieving less than 20% fade in specific energy after 500 cycles (144 Wh/kg).

Task Milestones and Progress

- Milestone 1 – Screen and establish standard cathodes and anodes for XFC with 50 meters double sides coated thick NMC electrode and graphite electrodes (11/15/18).
 - ✓ Completed
- Milestone 2 – Synthesize poly(LiMTFSI) of oligomers with 2~3 different degrees of polymerization (2/15/19).
 - ✓ Completed
- Milestone 3 – Finalize Gen 1 Hi-LiT electrolyte by screening conductivity of oligomers in 5 different solvent systems and 3 anion receptors additives (5/15/19).
 - ✓ In progress

Approach

Three highly interrelated approaches are implemented:

- (1) Innovative Li salt anion oligomers to suppress anion mobility and increase Li ion transference number. **We investigate** the oligomer form of anions to slow down the anion mobility, thereby increasing the Li ion transport portion in total current.
- (2) Formulations with multiple solvent systems to provide better Li ion mobility and suppress Li plating. **We investigate** the utilization of co-solvent systems for Hi-LiT electrolyte. This approach will further enhance the Li ion transport, facilitate fast charge-transfer due to less EC complexation with Li^+ and suppress Li plating due to improved anode resistance for long term cycling performance.
- (3) Anion receptor additives to further immobilize anions and dissociate cations in electrolyte. **We investigate** the addition of proper boron-based compounds with cavities suitable for trapping oligomer anion. The additive will further decrease the mobility of oligomer anions and increase the mobility of Li^+ by dissociating it from anions.

Technical accomplishments

High energy density Li-ion cell development using thick electrode

Anode:

94 wt% graphite (1520T, Superior Graphite)

5 wt% PVDF (KUREHA KF9300)

1 wt% carbon black (C-45 Timcal)

Areal capacity: 3.5 mAh/cm²

Porosity: 33%

Cathode:

94 wt% NMC622 (Targrey)

3 wt% PVDF (Solvay 5130)

3 wt% carbon black (C-45 Timcal)

Areal capacity: 3 mAh/cm²

Porosity: 30%

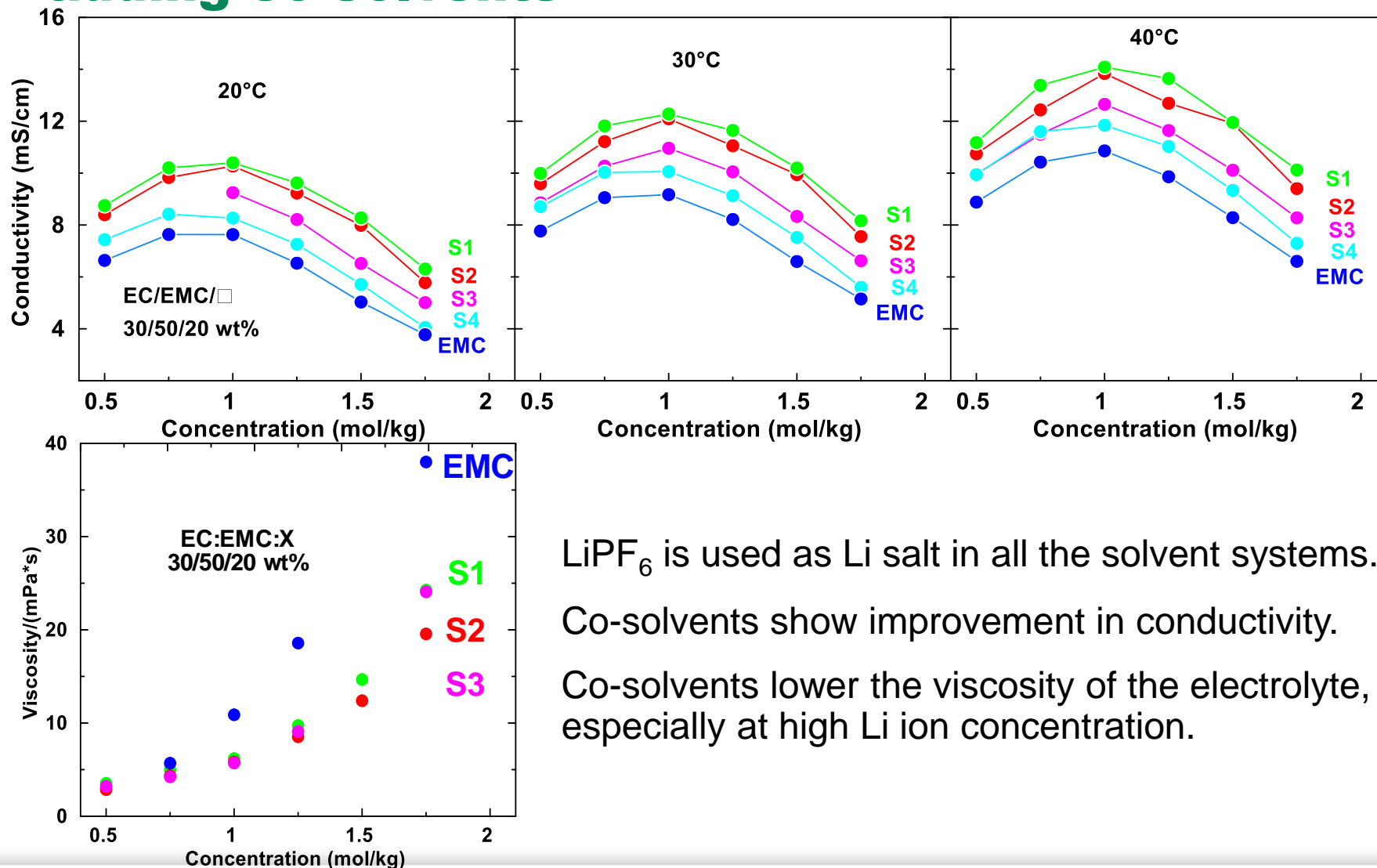
Baseline electrolyte: 1.2 mol/L LiPF₆ in EC/EMC 30/70 wt%

Cell cycling voltage window: 2.8-4.2 V

If scaled up to 2Ah cell, cell energy density ($\pm C/3$) is 210 Wh/kg.

Technical accomplishments

Ionic conductivity is improved by 10-33% with adding co-solvents



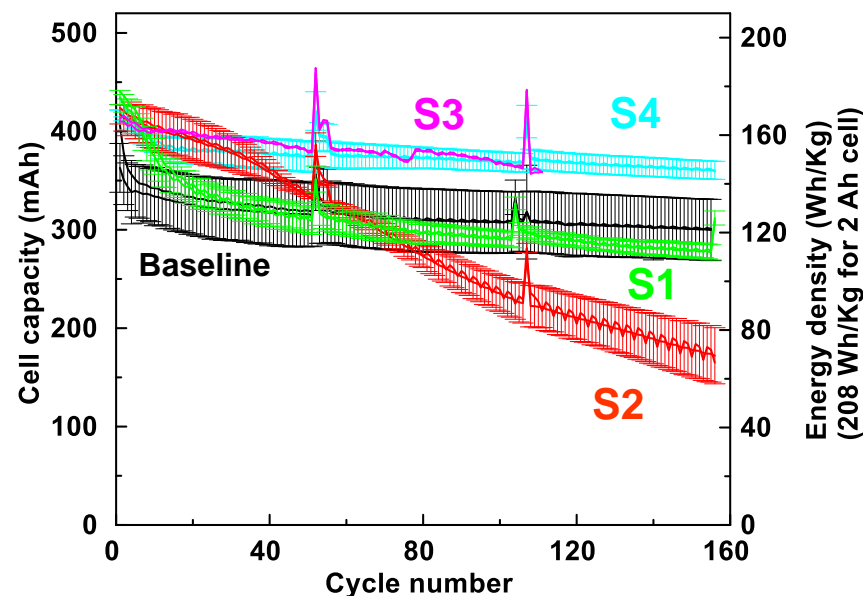
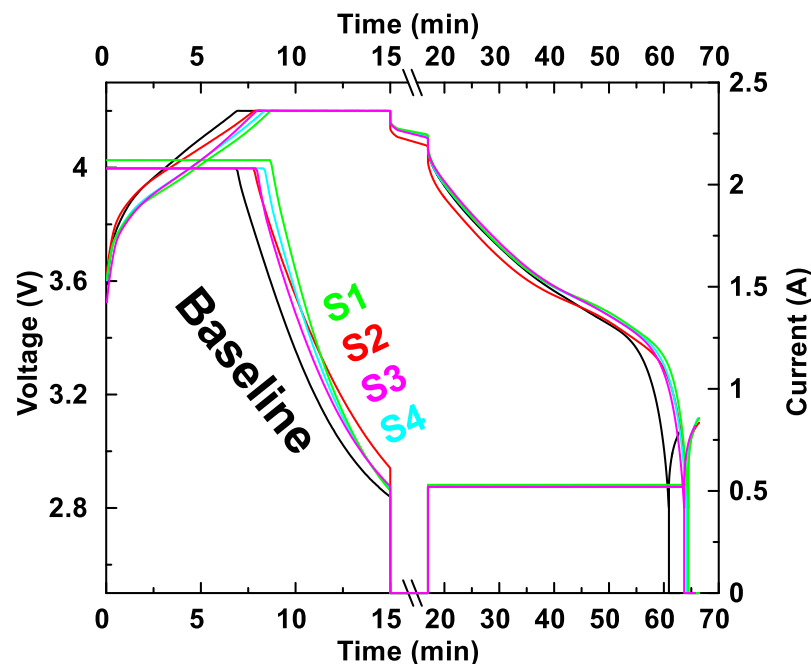
LiPF_6 is used as Li salt in all the solvent systems.

Co-solvents show improvement in conductivity.

Co-solvents lower the viscosity of the electrolyte, especially at high Li ion concentration.

Technical accomplishments

Five different solvent formulation show different fast charging effects



520 mAh pouch cell, cycling at +4C (15 minute)/-1C, voltage range 2.8-4.2 V.

All the co-solvents show higher initial fast charging capability.

S2 show capacity fading continuously afterwards. S1 shows the capacity fading in the first 20 cycles, but cell capacity was able to stabilize afterwards.

S3 and S4 shows higher fast charging capacity over cycling.

Technical accomplishments

Li plating exists in all the solvent systems and some co-solvents show different Li plating images from carbonate

Baseline



S1



S2



S3



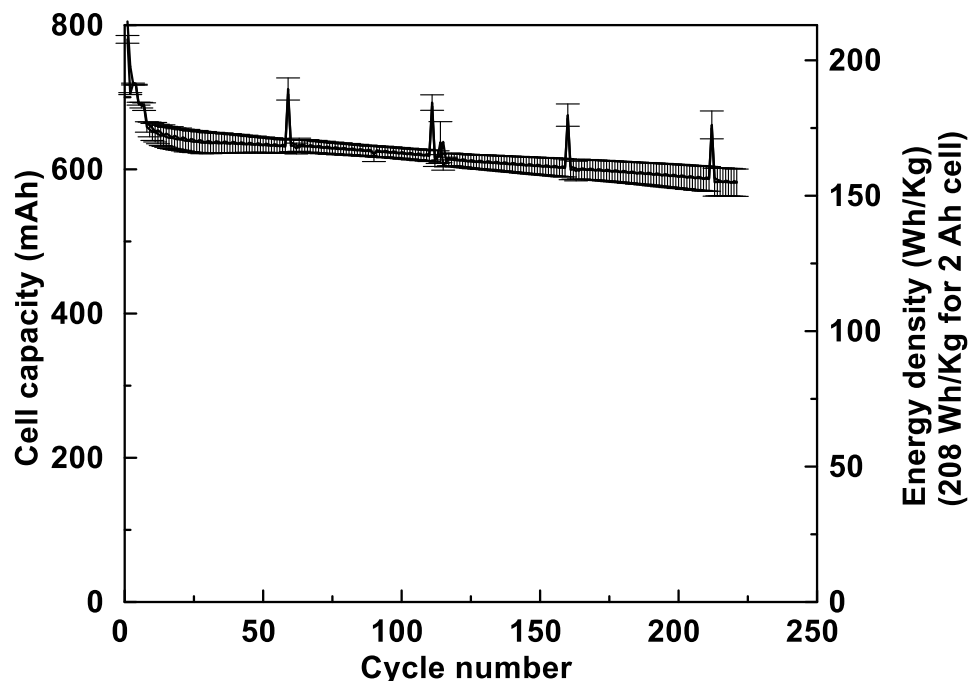
S4



All the five electrolytes show Li plating, with some having smooth/homogenous plating and some having inhomogeneous Li plating.

Technical accomplishments

780 mAh pouch cell scale-up with 20wt% co-solvent S4 shows very good cycling performance under 15-minute fast charging

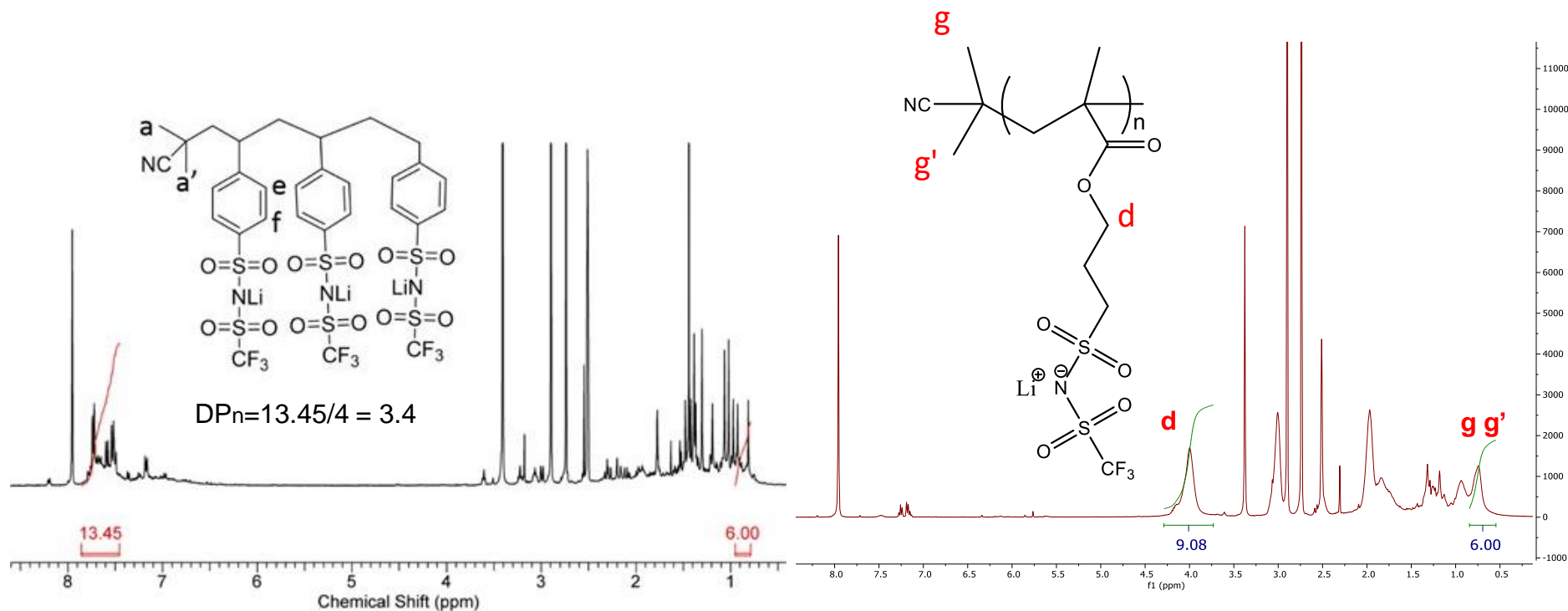


153 Wh/Kg of energy density after 200 15-minute fast charging cycles.

175 Wh/Kg of energy density if cycle under $\pm C/2$.

Technical accomplishments

Successful synthesis and characterization of oligomer and variation of the average DP_n



$AIBN:monomer = 1:1, DP_n = 3.4$

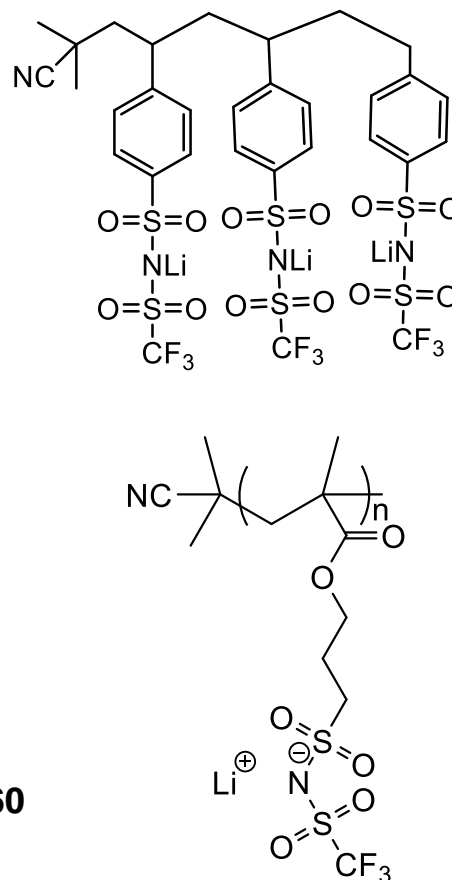
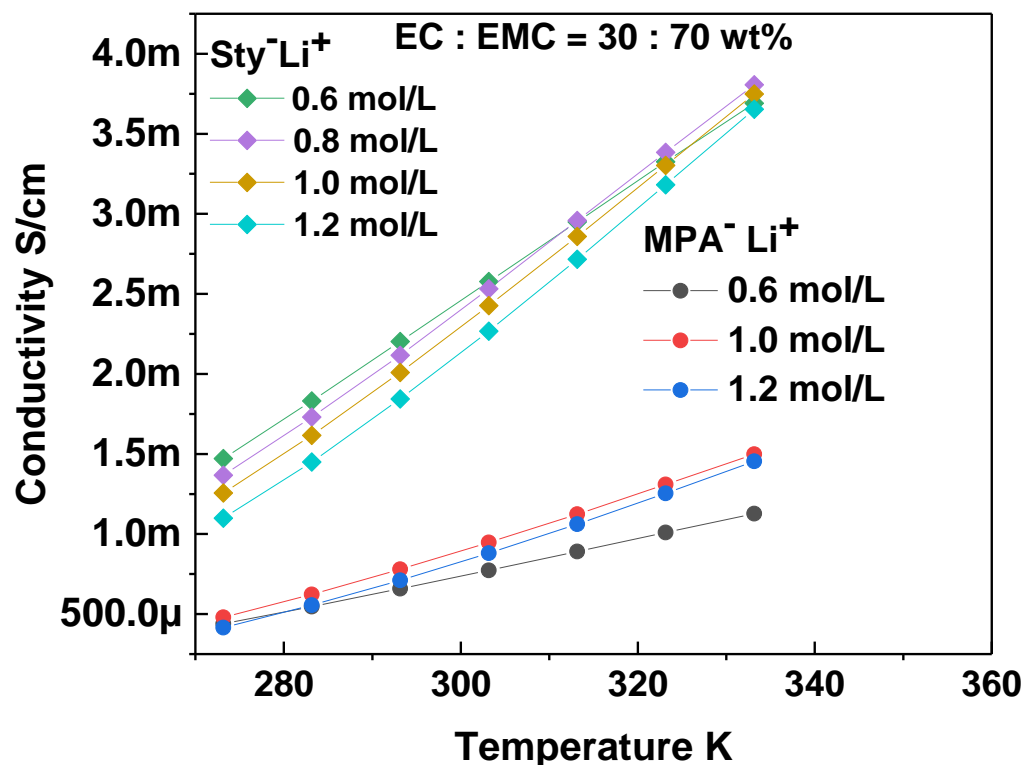
$AIBN:monomer = 1:2, DP_n = 4.0$

$AIBN:monomer = 1:3, DP_n = 5.4$

- Successful synthesis of different monomers and oligomer salts.
- Characterization of the structure using NMR and different DP_n were obtained.

Technical accomplishments

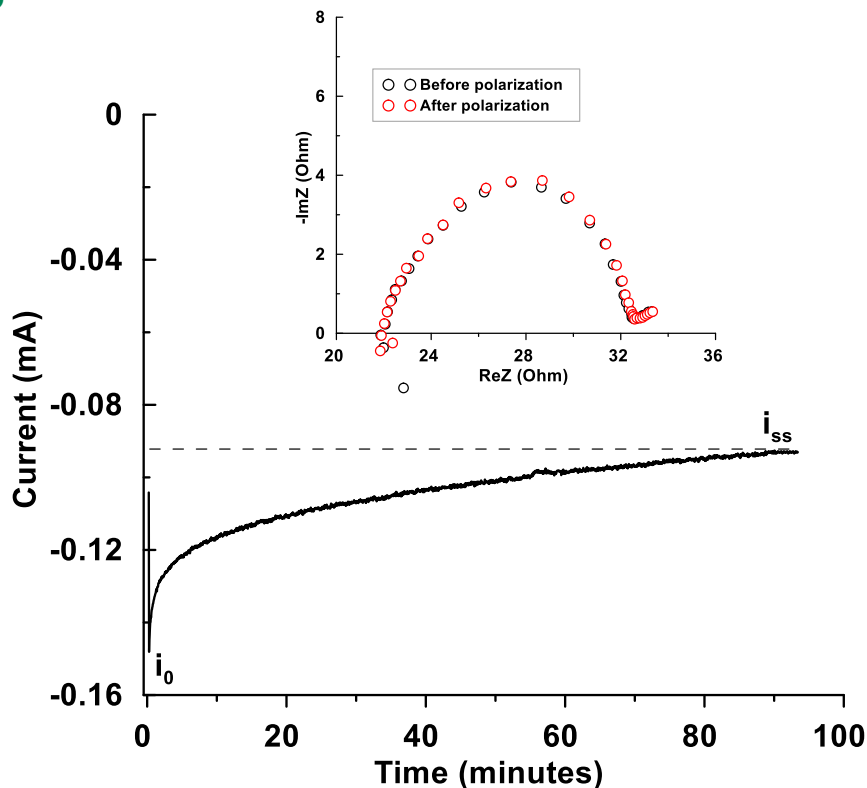
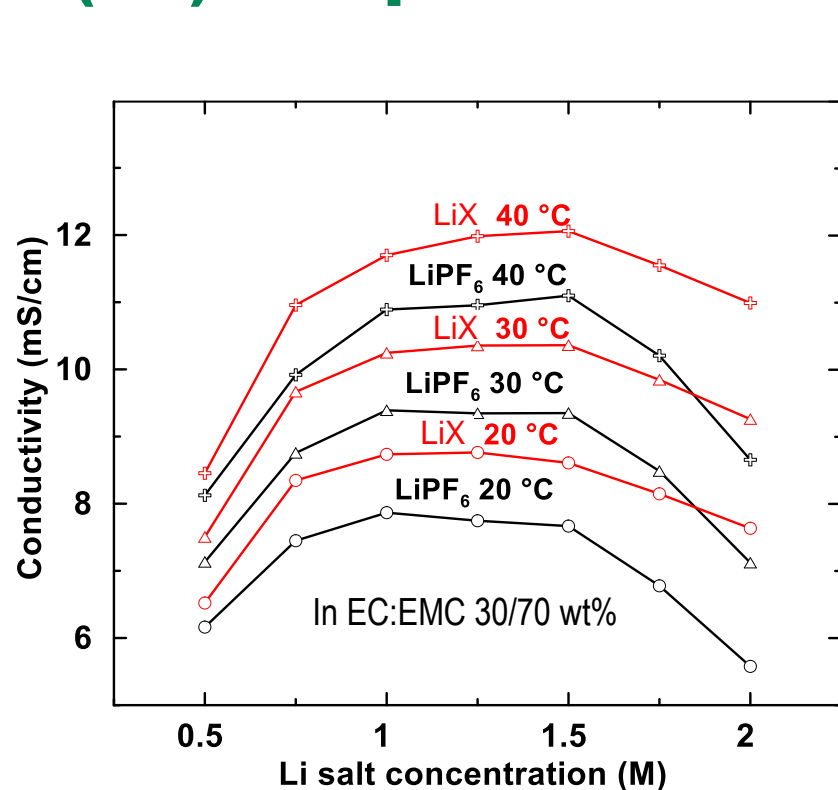
Conductivity of MPA-Li⁺ shows lower conductivity compared to Sty-Li⁺



The MPA-Li⁺ shows an order of magnitude lower conductivity compared to baseline electrolyte, and Sty-Li⁺ shows 4 times lower conductivity compared to baseline electrolyte.

Technical accomplishments

LiX salt shows higher conductivity and higher $t(\text{Li}^+)$ compared to LiPF_6

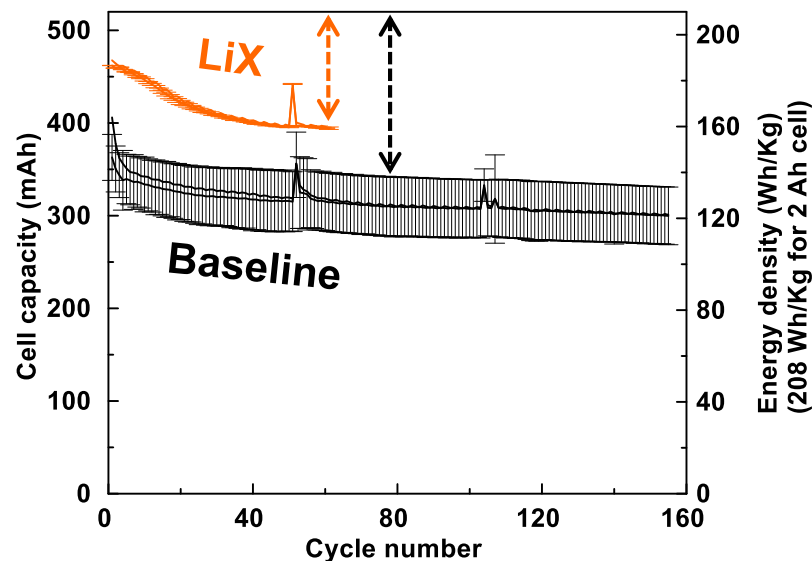
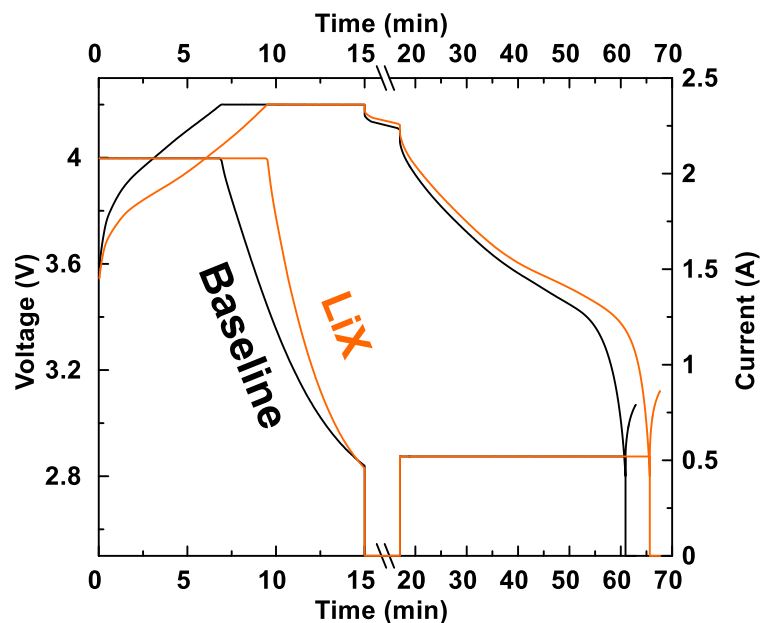


LiX shows 10% improvement in conductivity compared to LiPF_6 within the temperature range from 20-40 °C.

$t(\text{Li}^+)$ is 0.495, which is higher than 0.37 of LiPF_6 according to electrochemical measurement.

Technical accomplishments

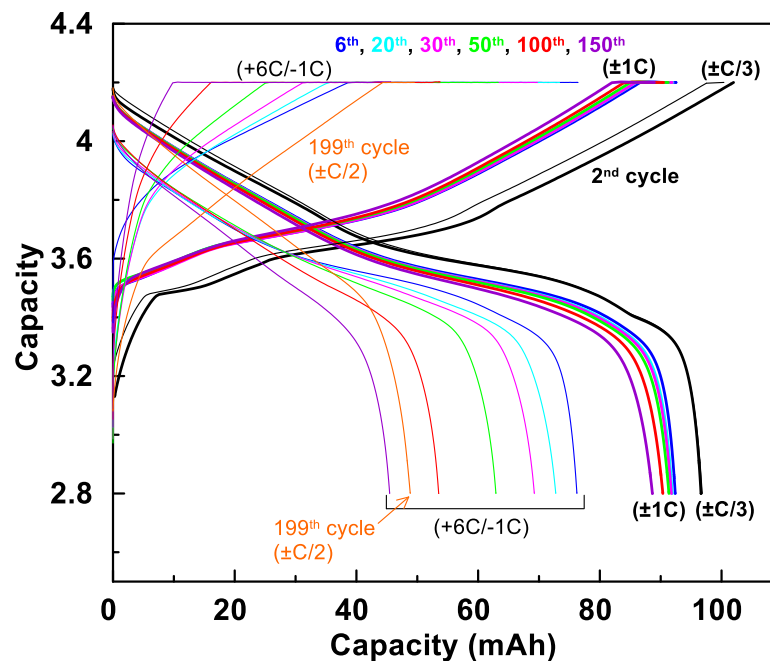
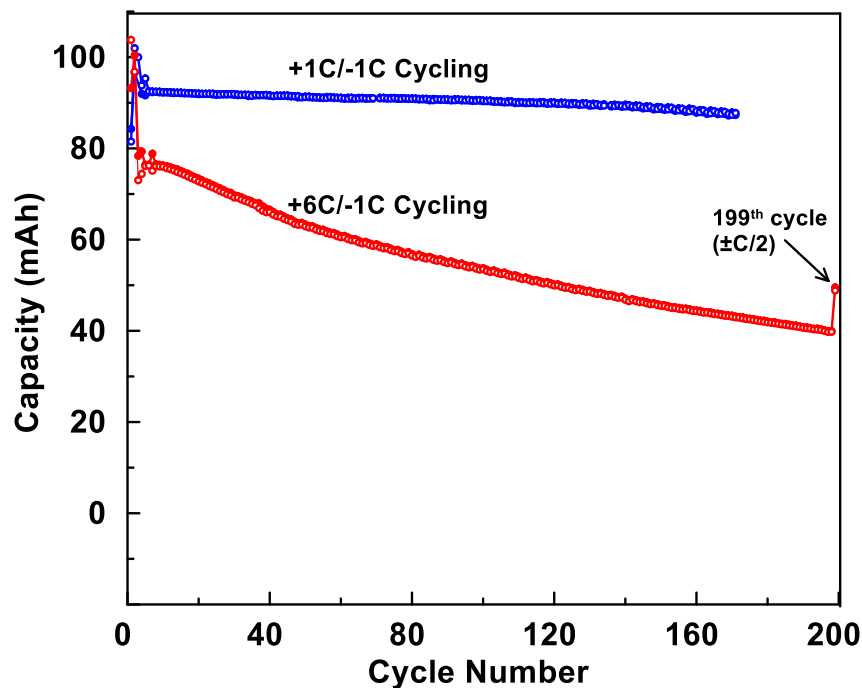
Li salt LiX shows higher initial fast charging capability and cycling is still ongoing



520 mAh pouch cell, cycling at +4C (15 minute)/-1C, voltage range 2.8-4.2 V.
Two cells with LiX salt are cycling with very similar behavior.
They show improved fast charging capacity with some capacity drop afterwards,
but still stabilized at higher capacity than baseline electrolyte.

Technical accomplishments

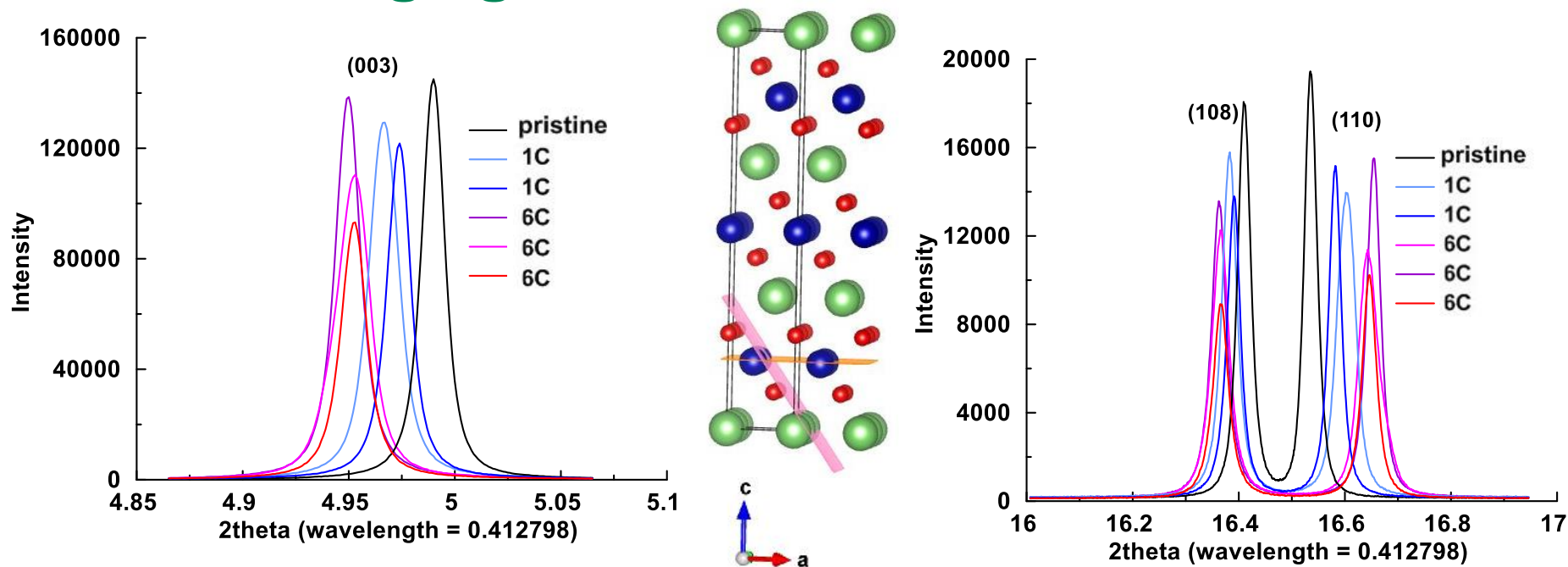
Understanding of the cathode structural changes after fast charging



Single unit pouch cell with NMC622/graphite electrodes, voltage range 2.8-4.2V.
Cells with fast charging cycling shows faster capacity fading.
The capacity is not restored after low rate C/2 cycle.

Technical accomplishments

Synchrotron XRD shows more c-axis expansion for fast charging cells



Cells were opened when discharged to 2.0 V.

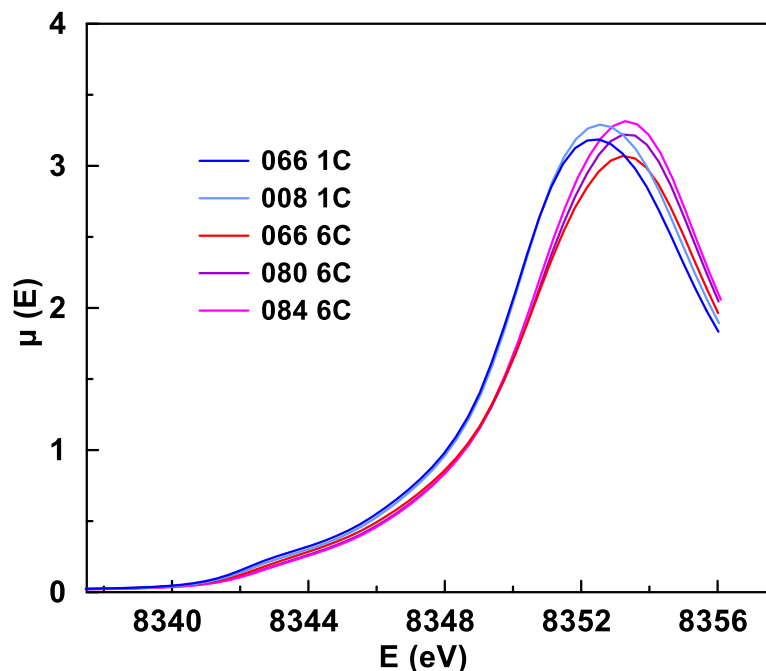
(003) Peak shifts to lower angle after 200 +1C/-1C cycles while shifts to further to even lower angle after 200 +6C/-1C cycles.

Further shifting apart between (108) and (110) is also noticed after fast charging cycles. Crystal unit cell expanded along c axis, indicating less lithium ions left in cathode after fast charging cycles.

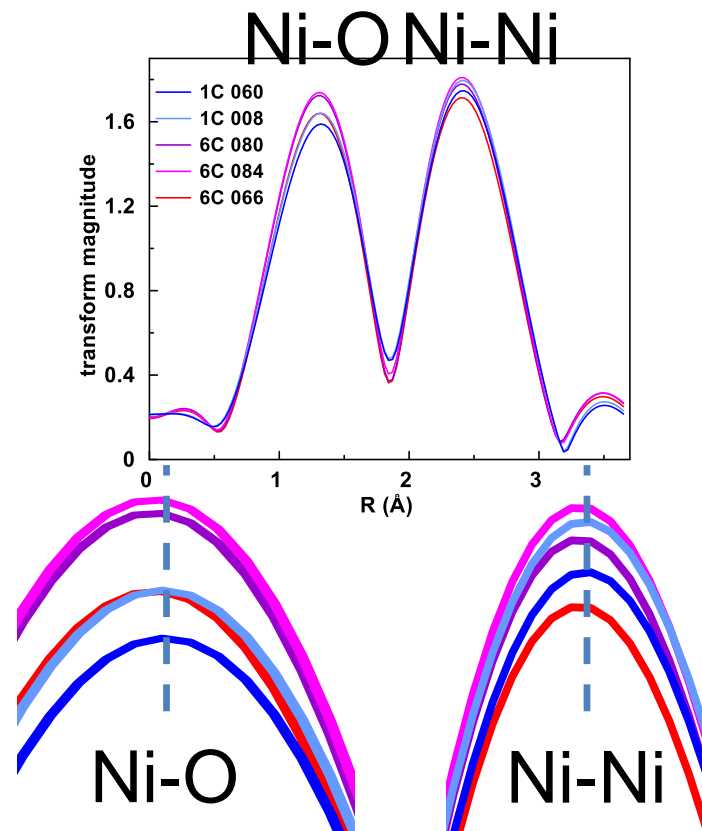
I. Belharouak et al. / Electrochem Comm 8 (2006) 329

Technical accomplishments

XAS shows higher oxidation state of Ni ion after fast charging cycles



Ni near edge XANES shows shifting towards higher energy after fast charging cycles, indicating high Ni oxidation state.



Both Ni-O and Ni-Ni peaks shifted to lower R values after fast charging cycles compared to those 1C charge, indicating a contraction in the Ni-O and Ni-Ni interatomic distances due to the higher oxidation of Ni ions.

Selected Responses to Specific FY18 DOE AMR Reviewer Comments

This project is kicked off
after 2018 AMR.

Proposed Future Research

- Further evaluation of more co-solvent on 10-minute fast charging vs baseline electrolyte.
- Purify and synthesize new Li oligomer salts with lower viscosity and higher conductivity.
- Study anion receptors on electrolyte structure and fast charging performance.
- Fast charging protocol optimization for higher energy density
- Post-mortem test of Li-ion cells after finishing fast charging cycles.
- Deliverables for 2 Ah cells.

Any proposed future work is subject to change based on funding levels.

Summary

- **Objective:** To implement a novel high-Li-ion-transference (Hi-LiT) electrolyte and enable a 10-minute charge of cells with 180 Wh/kg energy density by increasing t_{Li^+} from 0.36 to 0.75 while maintaining a relatively high conductivity of 4-10 mS/cm.
- **Approach:** (1) Innovative Li salt anion oligomers to suppress anion mobility and increase Li ion transference number. (2) Formulations with multiple solvent systems to provide better Li ion mobility and suppress Li plating. (3) Anion receptor additives to further immobilize anions and dissociate cations in electrolyte.
- **Technical:** Successfully synthesized oligomer type Li salts; studied four different co-solvents and effects on viscosity, conductivity and cycling performance; downselected co-solvents for future studies; established standard 3.5/3 (n/p) mAh/cm₂ electrodes for electrochemical testing; studied cathode structural change during fast charging; studied cell temperature change during fast charging.
- **Collaborators:** Guangsheng Zhang, UAH; Feng Lin, Virginia Tech; Michael Schulz, Virginia Tech; Kejie Zhao, Purdue; Jue Liu, SNS ORNL.

Acknowledgements



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- Team members:
 - David Wood
 - Tomonori Saito
 - Alexei Sokolov
 - Kris Inman (XALT)
 - Pengfei Cao
 - Xianyang Wu
 - Tianyi Liu
- Technical Collaborators
 - Guangsheng Zhang, UAH
 - Feng Lin, Virginia Tech
 - Michael Schulz, Virginia Tech
 - Kejie Zhao, Purdue
 - Jue Liu, SNS

Information Dissemination

Journal Papers and Presentations

- Z. Du, X. Wu, D. L. Wood III, K. Zhao, and I. Belharouak, Electrolyte Development and Its Application for Fast Charging of Li-Ion Batteries, 235th ECS meeting, Dallas, TX.
- Z. Du, D. L. Wood, I. Belharouak, Enabling fast charging of high energy density Li-ion cells with high lithium transport electrolytes, submitted.
- Shan Huang, Xianyang Wu, Gabriel M. Cavalheiro, Xiaoniu Du, Bangzhi Liu, Zhijia Du, Guangsheng Zhang, In Situ Measurement of Lithium-Ion Cell Internal Temperatures during Extreme Fast Charging, submitted.
- Tianyi Liu, Xianyang Wu, Feng Lin, Kejie Zhao, Michael Schulz, D.L. Wood, I. Belharouak, Zhijia Du, Effect of fast charging on the electrodes in Li-ion cells, in preparation.

Thank you for your attention!